

LATEST ADVANCEMENTS IN THE APPLICATION OF **ANALYTICAL SCIENCE** TO ANCIENT AND HISTORICAL **GLASS PRODUCTION**

ABSTRACT

Major recent developments in the archaeometry of ancient and historical glass production are outlined, and examples of methods which are set to determine the future agenda of glass studies are presented. In the past twenty years there has been a step-change in the quantity and quality of archaeometric data for glass production, allowing researchers to address larger-scale questions. Quantitative chemical analyses, including trace element analysis, are increasingly being used to reconstruct not only provenance, but also production techniques, contamination, and recycling; isotope analysis is being used to challenge previous assumptions about provenance and develop approaches more rooted in geochemistry; and novel analytical techniques including ToF-SIMS and portable laser ablation have great future potential if applied to the correct questions. Finally, the use of handheld, portable-XRF is increasing the range of questions that can be asked in the field, from production site survey to sample selection, and the analysis of *in situ* glass windows.

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INTRODUCTION

Recent years have seen a huge increase in the quantitative chemical analysis of glass from archaeological sites. I suggest that we have now reached a critical mass of data, opening up the possibility of doing much more than provenance studies with the results of chemical analysis.

At the same time, isotope and trace element analyses are further improving our picture of the provenance of vitreous materials, increasingly allowing us to provenance materials at a more local scale, and providing an insight into more difficult to detect patterns such as those resulting from glass recycling.

In this paper, I shall outline some of the major recent developments in the application of analytical science to questions of ancient and historical glass production, and highlight examples of research which is set to continue developing in the near future. Because much of the work covered by this paper is very recent, in some cases the critical publications have not yet been written and/or published, so references are to websites, posters, or awards rather than final published papers.

As the reader will appreciate, it is an exciting time to be involved in the analysis of archaeological glass.

QUANTITATIVE CHEMICAL ANALYSIS

A 'critical mass' of data?

In the past twenty years the application of scientific analysis to ancient and historical glasses has grown exponentially. A search for articles containing the keywords 'glass' and 'archaeology' using Web Of Science™ returns just 18 results for the years 1970 to 1997; compared with 164 for 1998 to February 2017. The situation is comparable, though somewhat less extreme, when we examine specifically archaeological journals. For the journal *Archaeometry*, there are 29 scientific papers explicitly dealing with man-made glass from the years 1970 to 1997, an average of one paper on glass for every two issues of the journal (0.5 glass papers per issue); and 85 for the years 1998 to February 2017, an average of 1.2 glass papers per issue; more than twice as many. Forty-nine of these papers were published in the past ten years, from 2008 to the time of writing (February 2017). That these metrics in part reflect a general increase in the publication of archaeological science does not detract from the fact that the increased published output in the field provides a far larger dataset upon which new research can build. In addition, continuing improvements in research methodologies, and the increased availability of techniques for quantitative chemical analysis mean that there are typically more samples reported per published paper, with some recent papers reporting on datasets in the hundreds (Schibille *et al.*, 2016; 2017; Phelps *et al.*, 2016).

Trace elements and provenance

Trace elements have long been recognized as a useful indicator of the provenance of ancient glasses, by linking the ratios of certain characteristic elements with localized geochemical information.

In a speech delivered in 1990, M.S. Tite argued that the "somewhat limited" impact of provenance studies on archaeology to that date arose, at least in part, because "the initiators fail to appreciate, or perhaps rather are unwilling to fully accept, the scale of the resources needed for and the scientific problems associated with such studies" (Tite, 1991). The location of raw materials sources, the possibility that different geographical sources have similar characteristics, and the potential alteration of an artefact's chemistry during production were

all cited as obstacles to provenance studies, and all are still relevant today. Nonetheless, significant in-roads have been made.

Although our understanding of the geology of potential areas of glass production is improving, the potential of glass to be traded over long distances can make provenance difficult for the reasons outlined by Tite (above). Several of the most significant archaeological attempts to 'provenance' glass in fact use a combination of archaeological evidence and chemical groupings rather than directly linking the chemistry of samples with local geochemistry.

Andrew Shortland used LA-ICP-MS in order to discriminate between trace element ratios in Egyptian and Mesopotamian glasses of the Late Bronze Age. The approach taken was led by the composition of the samples rather than the local geologies within the two regions. A set of trace and minor elements which were not associated with colorants was interrogated, and those which showed consistent correlations between the elements, and repeatable patterns between the glasses from the four sites, were identified as the most interesting (Shortland, 2007). The clearest discriminations came from Ti, Zr, La and Ce, which Shortland also notes are robust indicators in igneous geochemistry due to their resistance to low temperature alteration and weathering. Egyptian glasses are defined on this basis by a low Cr/La ratio combined with highly variable Zr/Ti ratios; Mesopotamian glasses by a high Zr/Ti ratio and variable Cr/La ratios [5]. It was noted that the glasses from the two Egyptian sites were compositionally indistinguishable from one another, as were those from the two Mesopotamian sites. This work enabled researchers to discriminate between Egyptian and Mesopotamian glasses traded into Mycenaean Greece (Walton *et al.*, 2009).

The analysis of complete beads by LA-ICP-MS, much of it conducted at the Field Museum in Chicago, has also been instrumental in discriminating between compositional types of glass forming part of the Indian Ocean trade, and within Africa. The advantage of the technique for this research question is that entire beads can be fitted into the sample chamber and ablated directly, requiring the removal of only the tiniest amount of material from the artefact.

The results have revealed changing flows of trade in the early second millennium AD, and significant links between southern Africa and the Indian Ocean trade (Dussubieux *et al.*, 2010; Robertshaw *et al.*, 2010), though more work will be required to establish the relationship between compositional subgroups and geographical locations, particularly within South and Southeast Asia. A comparison of LA-ICP-MS data from two different laboratories on 52 ancient beads demonstrated broad success in inter-comparability of results, but found that the heterogeneous distribution of some elements within glass, particularly colorants and opacifiers, impacted the results ((Dussubieux *et al.*, 2009).

ISOTOPE ANALYSIS

Radiogenic isotopes can be used to discriminate between various geological raw materials sources, and can thus be used as a key indicator of provenance in ancient and historical glasses. Isotope analysis combined with trace element analysis provides the most powerful combination of analytical tools available for determining the compositional grouping of archaeological glasses. In recent years, an increasing amount of geological reference data has been generated, but there is still a long way to go before we can truly address the problem of discriminating between large numbers of potential sources, not all of which yet have associated data, and which may be more heterogeneous than the (often limited) sampling implies. As with trace elements, in several cases isotopes have been used primarily to sub-divide glasses into groups, with the possible provenance of these groups being argued as much on the basis of the archaeological, as the geological evidence. Because we don't know,

in most cases, all the potential geological sources, this is rather important, as even a match between isotope 'signature' and source does not necessarily exclude the possibility that the sample in question could have come from an as yet unknown, isotopically similar source. Nonetheless, archaeological interpretations are tested or strengthened by the analysis of new isotope data, and several researchers are attempting to meet the required 'scale of resources' mentioned in Tite's speech (above). Examples of this will now be outlined.

Late Bronze Age glass

Oxygen, strontium and neodymium isotope analysis was applied to a series of Late Bronze Age glasses from sites in Egypt and Mesopotamia, to test the potential of these techniques for distinguishing between glasses from various sites. Oxygen isotopes were problematic to measure due to low yields in some of the samples, and because no significant variation was noted between glasses from different sites. Strontium isotopes were found to be more effective in discriminating between glasses, but were most useful when combined with neodymium. Researchers used Sr and Nd isotopes to discriminate between: an Egyptian group with relatively low Sr and Nd ratios; a group of glasses from Nuzi with high Sr and low Nd ratios; and a group from Tell Brak, with intermediate Sr and high Nd. While trace elements also provided a means to discriminate broadly between Mesopotamian and Egyptian glasses (see above), Nd and Sr isotopes seem to distinguish between production centers within Mesopotamia (Degryse *et al.*, 2010). Determining the meaning of these differences from a geological perspective is of course more challenging, as discussed below.

Isotope analysis can also be of use in determining the origins of certain glass colorants. Lead isotope analysis of a range of Egyptian materials of the Late Bronze Age, including yellow glasses colored and opacified with lead antimonate, revealed that lead metal and galena (a lead sulphide, PbS) may have been treated as separate commodities with different trade routes; lead metal being imported into Egypt, and galena being mined on the Red Sea coast (Shortland, 2006).

Roman and Medieval glass

A number of studies published in the early 2000s reported upon the uses of oxygen, strontium, neodymium and lead isotopes to distinguish different sources of raw ingredients employed in the production of Roman and medieval glasses, made with both mineral and plant ash fluxes (Henderson *et al.*, 2005; Freestone *et al.*, 2003; Leslie *et al.*, 2006).

Significant inroads into the geochemical basis for isotope provenance have been made by the ERC-funded ARCHGLASS Project, which involved a large-scale investigation of potential sources of coastal glassmaking sand for the Hellenistic and Roman periods, investigating both trace elements and isotopes (Degryse, 2015). Based on the analysis of 77 beach sands from Spain, France and Italy, it was shown that a due degree of caution is required when interpreting the results of Sr isotope studies, as not only the lime content, but also the silicate fraction of the sand can influence the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The results are promising, however, demonstrating a distinction between East and West Mediterranean sands: the Nile sediments which dominate the eastern Mediterranean have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the very radiogenic, silicate-derived Sr in the West Mediterranean (Brems *et al.*, 2013). For neodymium, there is also a distinction between the Nile-dominated East Mediterranean signature ($> 6.0 \text{ } \epsilon \text{ Nd}$) and the West Mediterranean or European one ($> 7.0 \text{ } \epsilon \text{ Nd}$) (Degryse & Schneider, 2008), and it is suggested that the most effective combination for providing provenance information for Roman glasses is to be sought in a combination of the Nd isotope

analysis, and trace element analysis (Brems & Degryse, 2014). Despite the sizeable contribution of this work, much remains to be done, and it is worth noting that the researchers were unable to collect and analyze sands from the North African coast, Corsica, Sardinia, Greece, Turkey or Cyprus.

Most recently, the use of boron isotopes was tested as a means of discriminating between the relatively few known sources of mineral soda accessible to the Romans ('mineral soda' is preferred here over the commonly employed terms 'natron' or 'trona', as the composition of the minerals can vary widely). Most of the B enters the glass via the flux, although both sands and shells could also affect the $\delta^{11}\text{B}$ values. The study compared 33 samples of Greco-Roman glass with 18 samples of natron, from locations in Egypt, Libya and Greece. The $\delta^{11}\text{B}$ values for the glasses ranged from +26 ‰ to +34 ‰, averaging at +29 ‰ (uncertainty 1.6 +29.8 ‰, $k=2$). The average is a close match for the values obtained for mineral soda samples from Wadi Natrun (+29.8 ‰), and al-Barnuj (+28.5 ‰), both in Egypt. The four samples from Fazzan in Libya (average +25.3 ‰) also show some overlap with these ranges. The study demonstrated that it is unlikely the Lake Pikrolimni site in Greece was exploited for this purpose, as the values of these samples were much lower (+10.5 ‰) (Devulder *et al.*, 2014).

From Medieval to Early Modern Glass

As the application of isotope studies to glass moves out of its infancy, it is becoming increasingly possible to distinguish between centers of glass production at a more local level. In a study using Sr and Nd isotope analysis in combination with EPMA, to investigate the production of English 'forest glass' from the 14th to 16th centuries, Andrew Meek and colleagues were able to differentiate regionally between glasses from the two main locations of medieval English glass production, the Weald and Staffordshire, but crucially, they were also able to identify differences in the glasses from individual production sites, based on the analysis of five samples each from four different production sites, in two different regions (Meek *et al.*, 2012).

THE APPLICATION OF NOVEL ANALYTICAL TECHNIQUES

In addition to the ongoing development of existing analytical techniques, there is always the possibility of applying new techniques, or techniques not previously used by archaeologists. In some cases, as with the use of portable laser ablation discussed below, these may hold great potential for the future. In others, as with the case of ToF-SIMS (also discussed below), applications for the analysis of glass production may be more limited, but are no less valuable for it. It is crucial that we tailor the techniques used to the archaeological questions being asked of the material.

ToF-SIMS

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a variant of the Static SIMS technique, which uses a pulsed ion beam to remove molecules from the top few atomic layers of a sample. These are accelerated through a field-free drift tube and their masses determined by their flight times. ToF-SIMS is a surface analysis technique, with high lateral and depth resolution, and powerful imaging capability. Samples can be semi-quantitatively analyzed and their compositions mapped.

Except for studies focusing on corrosion, surface analysis techniques have found few applications in archaeological glass science to date. The unique combination of lateral and depth resolution in ToF-SIMS, however, makes it the ideal technique for the analysis of small

inclusions in ancient glasses which were used to render them opaque, because it allows the researcher to distinguish between the chemistry of the inclusion itself, and that of the glass matrix which surrounds it and lies beneath it, and to map the interaction between the two.

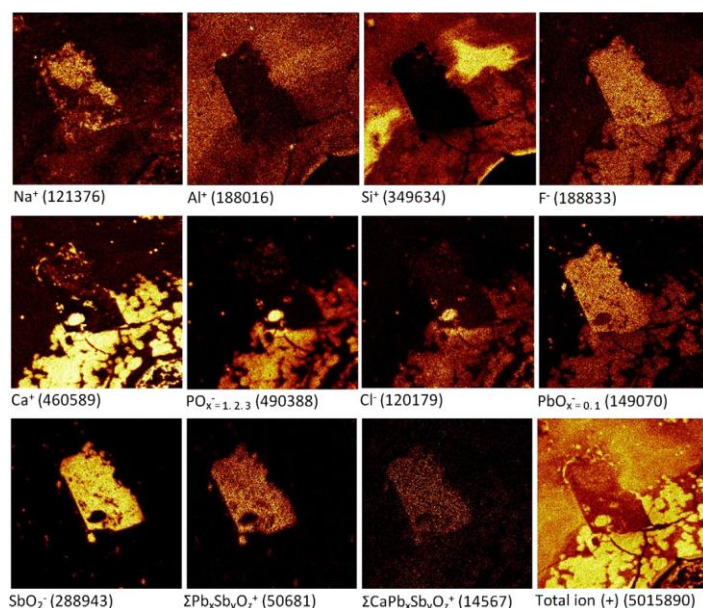


Fig. 1: Positive and negative secondary ion maps for an 80 x 80 μm area of a corroded, opaque yellow sample from Thebes, Greece.

Two pilot studies have been undertaken to date on this application of ToF-SIMS to polished sections of archaeological glasses (Duckworth *et al.*, 2012; Rutten *et al.*, 2009). As shown in Fig. 1, the mapping capabilities of the technique provide unique information on the technology of glass opacification, in this case for an opaque yellow glass from Mycenaean Thebes, Greece. The image shows a sample that was ground and polished prior to analysis (avoiding the risk of surface contamination). Positive and negative ion maps show a large, straight-sided, lead antimonate inclusion with clearly defined edges, some of which appear to have been partially dissolved into the surrounding matrix, perhaps accounting for the numerous smaller inclusions which are also elevated in Sb and Pb. This combination of features implies that the lead antimonate opacifiers were added to the glasses at a relatively low temperature and never fully dissolved, providing a direct insight into the production technology of the glass. Also visible is what appears to be an area of corrosion surrounding a void, on the bottom right of the images.

Future research might focus upon the potential of ToF-SIMS to provenance the opacifying inclusions. If inclusions such as the one shown in Fig. 1 were indeed added at a low temperature and never fully dissolved into the glass melt, then trace elements associated with these would be indicative of their provenance, offering insights into Late Bronze Age trade systems, and the value of colored and opaque glass.

Handheld laser ablation

As noted above, one of the advantages of laser-ablation coupled with ICP-MS is that, for those items small enough to fit into the sample chamber, the analysis is all but non-destructive (sometimes referred to as 'quasi non-destructive'): the damage caused by the laser is barely visible with the naked eye. Furthermore, surface contamination or corrosion effects, which hamper non-invasive techniques, can be dealt with by sputtering away the first few layers of material.

Nonetheless, these advantages are not available for the analysis of larger objects which cannot fit into the sample chamber or be subject to destructive sampling, and neither are they an option for in situ or protected materials, which cannot be removed for analysis.

The development of portable laser ablation looks set to meet these challenges. Unlike handheld pXRF, the analysis itself is not conducted in the field: the device in question samples materials in the field and stores them for analysis under laboratory conditions. Its applications to archaeology have been limited to date, but they are being developed (Glaus et al., 2012; NEXUS 1942). It is hoped that in future this technique will further increase our dataset by allowing us to work with objects which are otherwise inaccessible, either because they are too fragile, or because of local laws which prohibit removal for analysis.

LARGE DATA SETS AND SECONDARY PRODUCTION EFFECTS

As has already been shown, the development of analytical techniques and methodologies has a huge role to play in the social interpretation of ancient and historical glass production. Equally significant, however, are the changing ways in which data generated by traditional analytical techniques can be reinterpreted, or turned to new questions. Here, inroads are being made in two fields: the collation and analysis of compositional data from numerous published studies; and an increasingly nuanced understanding of the role of production methodologies, and contamination during production, on the final composition of glasses.

Large datasets as a resource to redefine compositional groupings, and recycling

Archaeological glass researchers have been attempting to combine existing datasets for years, but thanks to the afore-mentioned 'critical mass' of quantitative archaeometric data for glass compositions, and to the ongoing re-definition of compositional categories, it is now possible to ask far more nuanced questions than was previously possible.

The hazards of comparing analytical data from different laboratories and experimental set-ups have been acknowledged for as long as the attempt to compare results across datasets has been made, though they have not always been rigorously applied. When comparing between datasets, it is important to select only publications for which an appreciable level of metadata is available, and to compare only between quantified (not semi-quantified) results. Comparison between the ratio of different elements or groups of elements is more robust than comparison between absolute quantities of a given element, as the latter may be distorted by differences in experimental set-up, standardization and normalization practices, and the selection of elements analyzed.

Elisabetta Gliozzo (2016) recently published the results of collating 1496 analyses of colorless glass, to refine understanding of colorless glasses from geographical, typological, chronological and compositional perspectives. She defined four key compositional groups on the basis of their de-colorant (Mn and Sb) quantities, and identified long-term patterns in the use of various raw ingredients.

Ongoing work into refining our understanding of glass compositional groups is also leading to the increasing ability to detect the effects of recycling. 'Intermediate' compositions, which lie between two well-established and well-defined compositional groups, are commonly interpreted as being indicative of recycling (Gliozzo, 2016). Caroline Jackson and Sarah Paynter have demonstrated extensive evidence of recycling in 1st-4th century Roman glasses from Coppergate, York. This is most clearly recognized through the presence of the two glass de-colorants, Mn and Sb, in the same sample (Jackson & Paynter, 2015). At Coppergate, mixed Mn and Sb glasses made up 40 % of the assemblage.

To clarify the finding, it should be noted that this result illustrates that a minimum of 40 % of the glass was probably recycled (assuming Mn and Sb were not entering the glass together). It is likely, however, that over 40 % of the glass had been recycled at some point, but that this was less visible due to the practice of recycling 'like with like' (e.g. Sb-decolored glass with Sb-decolored glass).

This may help to explain why evidence for recycling increases over time from the first century AD, because with each generation of glasses, the chances of a small amount of differently-composed glass entering the mix and becoming 'visible' to the archaeometrist, are increased. As noted by Jackson and Paynter themselves, changing scenarios of glass production and supply would also have had significant effects on the range of choices open to those practicing glass recycling.

These ideas are the subject of an ongoing research project by the author of this paper, which seeks to trace incremental effects of recycling over large datasets, and which considers a wide range of glass colors and types, to account for the fact that glass is often transmuted during recycling from one form to another. For example, the microscopic and compositional analysis of Islamic glass bangles from Libya revealed extensive signs of recycling. The bangles may be the 'end point' of the practice of recycling vessels and other objects, when glass is highly contaminated and its composition too unpredictable for glass blowers. The intensive coloration of the bangles would have served to mask the visual appearance of these effects, while their thick forms and relatively low-temperature production techniques required less control and prior compositional knowledge than was demanded by glass blowing (Duckworth *et al.*, 2016).

Experimental and analytical work on the contamination of glass batches during production

In addition to alterations in glass composition through mixing different glasses during recycling, as outlined above, the re-melting of glass may introduce other contaminants which can be detected by compositional analysis, and which must be accounted for in any compositional interpretation. A significant amount of our understanding of these processes comes from the work of Sarah Paynter.

In the afore-mentioned study of glasses from Roman Coppergate, York, evidence was found for the contamination of the glass during recycling, by ceramic crucibles and furnace structures. The authors point out that, once contaminated, a colorless glass would be more likely to be re-mixed with blue-green glass types (Jackson & Paynter, 2015).

Paynter had previously analyzed a quantity of production remains from the experimental reconstruction and operation of a Roman glass workshop undertaken by Mark Taylor and David Hill in 2005 and 2006 (Taylor & Hill, 2008; Paynter, 2008). In one part of the experiment, raw ingredients were added to a large pot (crucible) to produce a primary glass, and samples were taken from this at 14, 29, 54, 76 and 90 hours after initiating the firing. The quality and homogeneity of the glass broadly improved over heating time, but continued heating also saw an increase in the potash content of the glasses, due to contamination from the alkali-rich gases emitted by burning the wood fuel (Paynter, 2008). Contamination from fuel ash was also described in some glasses which spilt into the firing chambers of the furnaces, illustrating the difficulties with assuming that the composition of waste glass found at production sites is necessarily reflective of the composition of materials made there. Similar considerations apply to glass adhering to crucibles, and to glazes formed on furnace walls. Contamination by alumina from clays, iron from tools, alkalis from the fuel gas, and lime from the fuel ash all need to be considered when interpreting the results of the compositional analysis of glass.

NEW USES OF HANDHELD PORTABLE-XRF IN THE FIELD

As noted by Thilo Rehren and Ian Freestone, in their recent review of the archaeometry of glass, in some cases, “the increasing availability of analytical equipment poses new challenges” (Rehren & Freestone, 2015). They are referring to the increasing use of handheld portable XRF in the field. Many researchers feel that the easy accessibility of this analytical technique is a danger, as the generation of results is open to non-experts, who may not understand the limitations of the data. Nonetheless, and as Rehren and Freestone go on to discuss, handheld pXRF has great potential in glass studies, when its limitations are properly taken into account.

One of the advantages of handheld pXRF is that it can be used to rapidly analyze large assemblages of glass at low cost. Although it cannot substitute for destructive, fully quantitative analysis in characterizing glasses, or comparing results between datasets, it does have the potential to define broad compositional groups within a larger pool of data, facilitating on-site sampling strategies, as being tested by Daniela Rosenow and Thilo Rehren for glasses from Bubastis, Egypt (Rosenow & Rehren, 2014).

Handheld pXRF can also be used to generate information in its own right, as shown in two recent examples of its development: as a geochemical tool to help locate glass production sites; and for the *in situ* analysis of historic window glass.

In geochemical survey of production sites

The use of handheld pXRF in geochemical survey was developed in search of metallurgical production activity, as part of the Sintashta Collaborative Archaeological Research Project (Hanks *et al.*, 2014.; Donan *et al.*, 2014). The principles of the technique were also adopted by the Madinat al-Zahra Survey Project, from 2015 to 2016, where it was used reflexively with magnetometry.

In the latter project, the technique was coupled with geophysical survey techniques including magnetic susceptibility and magnetometry. The underlying rationale of the project is that pyrotechnological activities, including glass and glazed ceramic production, would leave heavy metal traces in the soil. Its aim was to test the combination of geophysical and geochemical techniques for locating pollution associated with high temperature production within the 10th century Islamic city of Madinat al-Zahra, Córdoba, Spain (Duckworth, 2012). The site is a good candidate for this combination of techniques. It was never built upon following its abandonment and destruction in the early 11th century, and today is protected land which has not been ploughed in over 100 years. Furthermore, there was some hope that the technique would help to identify the workshops in which the famous Madinat al-Zahra ‘green on manganese’ glazed ceramics were produced.

Using a GPS to rapidly locate points on the site grid, XRF readings were taken at the soil surface at 20 m intervals (and in areas of special interest, 5 m and 10 m). The relative intensity of key heavy metal markers was plotted, revealing ‘hot spots’ of pollutants (Fig. 2). These same locations were shown by magnetometry to feature structured magnetic anomalies, probably associated with pyrotechnological activity. Although the results remain inconclusive and have not yet been subject to ground-truthing by excavation, it is interesting to note that the elevated metals – Pb, Cu and, nearby, Mn – were all associated with the production of the period’s well-known glazed ceramics. At the least, this demonstrates the efficacy of geochemical prospection by handheld pXRF in seeking, not only the remains of metallurgical activity, but those of vitreous materials production as well.

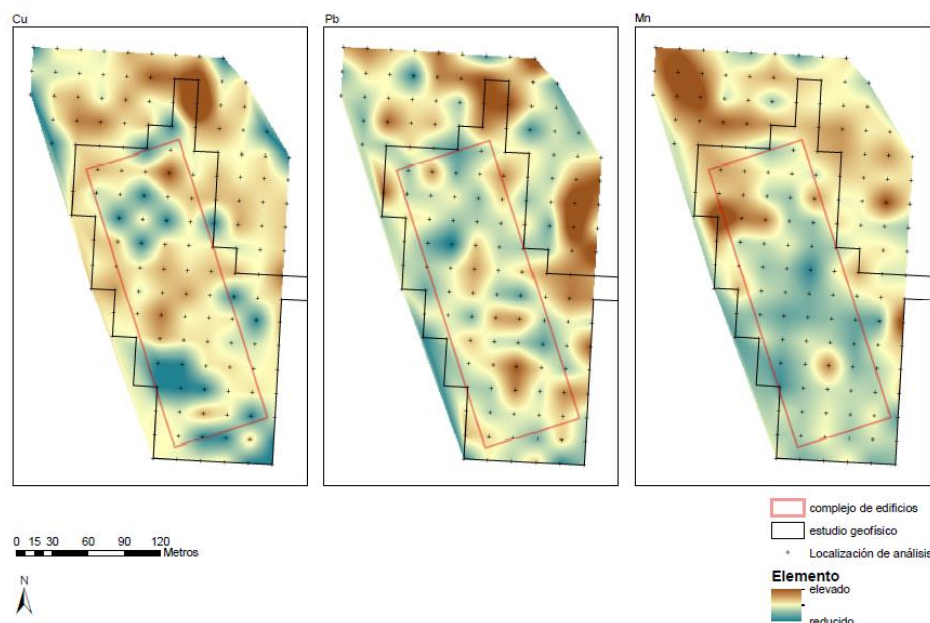


Fig. 2: Results of handheld pXRF analysis at Madinat al-Zahra, 2015, showing brownish-colored 'hot spots' of Cu (left), Pb (center) and Mn (right).

In the analysis of historic windows

Window glass is well-suited to pXRF analysis, as it is relatively homogeneous, and – crucially – flat. David Dungworth has developed the use of handheld portable XRF in the analysis of historic windows. His technique employs a helium gas flush, to improve the detection of lighter elements (Mg to P), and is focused on rapid data collection, with a low acquisition time (30 s). A large numbers of glass windows were analyzed in situ at Walmer Castle and Ightham Mote in Kent, and Thornhill Parish Church, West Yorkshire: 2716 windowpanes in total.

Dungworth (2012) notes the discrepancy between the time required for data collection, which can be very rapid (2000 panes were analyzed at Ightham Mote by up to five people, over five days), and the much longer time which must be allowed for data processing and interpretation of the results.

Using this method, and by comparison with laboratory-established compositional groupings, changes in composition over time can be compared with new pXRF readings to assign in situ glass windows to broad dating brackets (before c. 1567; 1567-1700; 1700-1835; 1835 onwards) (Dungworth, 2012). Drawbacks include the thinness of glass windows, which can affect the quality of results, difficulties in measuring light elements, and the surface effects of corrosion.

One of the outcomes of this research was Dungworth's demonstration that some of the difficulties in detecting light elements can be offset by focusing instead on differences in related heavier elements, present in smaller quantities (Dungworth, 2012; 2016) These findings have more recently been used in the analysis of thirty window glass pieces from the Great East Window in York Minster, dated 1405-1408 (Adlington & Freestone, 2017).

Fragments of some of the samples were also analysed quantitatively by EPMA, and comparison of the results revealed a systematic error in the pXRF results, ascribed not to problems with the application of the technique (which worked well for a glass standard), but to the presence of a thin layer of surface corrosion on the windows themselves. The paper's

authors, Laura Adlington and Ian Freestone, note that the depth function is logarithmic, and so for the lighter elements c.99 % of the emitted X-rays will originate from the shallower layers, meaning that a corroded, leached layer of altered composition, even if very thin, will have a notable effect on readings for the lighter elements [40]. Because the X-rays for heavier elements are generated from deeper within the glass, however, due to their higher energy, the researchers made useful comparisons between Rb, Sr and Zr, which in the case of Rb and Sr acted as proxies for the lighter elements in the same groups. As noted by Adlington and Freestone, “the analyses of selected, relatively heavy, trace elements hold the most promise for a study of medieval glass by pXRF – they are analysed well due to their higher-energy characteristic X-rays, and should relate information about the raw materials in the same way that the major elements do” [40]. Differences in Rb and Sr were thought to be indicative of different glass batches. Differences in Zr, indicative of the sand component of the glass batch, were sensitive to the different glassmaking regions from which the glasses were sourced.

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